Amendments to the Specification:

Please add the following paragraphs after paragraph [0060]:

Preparation of Monodisperse Semiconductor Nanocrystals (NCs)

[0061] In the growth of compound semiconductor NCs, the requisite supersaturation and subsequent nucleation can be triggered by rapid injection of metal-organic precursors into a vigorously stirred flask containing a hot (~150–350°C) coordinating solvent. The solvents usually used are mixtures of long-chain alkylphosphines R_3P, alkylphosphine oxides R_3PO (R = butyl or octyl), alkylamines, etc **(17)**. In the synthesis of II-VI NCs (ME whereM = Zn, Cd, Hg; E = S, Se, Te), metal alkyls (dimethylcadmium, diethylcadmium, diethylzinc, dibenzylmercury) are generally selected as the group II sources. The group VI sources are often organophosphine chalcogenides (R_3PE) or bistrimethylsilylchalcogenides TMS_2E (TMS, trimethylsilyl) (where E = S, Se, and Te). The R_3PE class of reagents is usually preferred as Se and Te sources because they are easy to prepare; TMS2S is selected as the S source because it is more reactive than R_3PS and is commercially available. The use of mixed precursors, for example a combination of Se and S precursors, leads to the straightforward production of alloys, although the NCs' stoichiometry does not directly reflect the precursor ratio, but rather the differential rate of precursor incorporation.

[0062] Growth of II-VI NCs is not limited to the use of R_3P and R_3PO as high boiling coordinating solvents. Injection of reagents into hot alkylphosphites, alkylphosphates, pyridines, alkylamines, and furans all produce NCs. Mikulec recently demonstrated that using alkylphosphoramide-tellurium precursors, in lieu of R_3PTe, produces CdTe NCs with much higher luminescence efficiencies **(18)**.

The strong interaction of R_3PO with Zn precursors unduly retards the growth of

ZnE NCs. Although R_3P may still be employed, Guyot-Sionnest and co-workers

found that using alkylamines as the coordinating solvent greatly enhances the

growth rate of ZnE NCs **(19)**.

[0063] Similarly, synthesis of high-quality InP and InAs NCs has been achieved by

rapidly mixing and heating of III and V precursors in high boiling, coordinating solvents.

Preparations of InP and InAs NCs are now capable of yielding samples with

$\sigma \le 10\%$. Typically $InCl(C_2O_4)$ is employed as an In source with TMS_3P or

TMS_3As in R_3P/R_3PO solvents (20–22). In these III-V preparations the In precursor

is present in the hot solvent prior to the injection of TMS_3P or TMS_3As. Growth

of the NCs is slow since Ostwald ripening over 1 to 6 days is required to reach

the desired NC size. A wealth of other potential organometallic precursors and

high-boiling coordinating solvents remain untested, thus providing opportunities

for continued expansion to new NC systems.

Preparation of Monodisperse Metal NCs

[0064] The synthesis of metal colloids has been studied for over a century and yet the number of

preparations yielding a size series of monodisperse metal NC samples is surprisingly small. The

most established methods involve aqueous reduction of metal salts (notably Au or Ag) in

the presence of citrate anions **(23)**. These colloids are electrostatically stabilized by

the adsorption of ions to the NCs' surfaces during growth. These samples have long

been referred to as monodisperse, although in general $10 < \sigma < 15\%$. Flocculation

of these colloids is irreversible, preventing further processing to achieve the desired

$\sigma \sim 5\%$. Chemisorption of organic ligands on the surface of metal NCs is essential

to permit further handling. Schmid provides an excellent overview of the advances

in metal colloid synthesis **(24, 25)**.

[0065] A two-phase reduction method, described by Brust, Schiffrin, and co-workers,

when coupled with size-selective processing produces capped Au and Ag NCs with

$\sigma \sim 5\%$ **(26)**. In general, aqueous metal salts (e.g. $HAuCl_4$, $AgNO_3$, $AgClO_4$) are

mixed in a toluene solution containing long-chain alkylammonium surfactants to

form a two-phase system. Vigorous stirring for 1 to 3 h transfers the metal salt

into the organic phase, which is then separated. A measured quantity of capping

agent, typically a long-chain thiol, is added to the solution while stirring, and then

a reducing agent (e.g. $NaBH_4$ or hydrazine) is rapidly added to nucleate NCs. The

average NC size is coarsely tunable by adjusting the ratio of capping groups to

metal salt, whereas size-selective precipitation is employed to narrow the initial

size distribution. Several studies have refined the preparation of thiol capped Ag

and Au NCs **(27, 28)**.

[0066] The preparation of metal NCs in inverse micelles warrants mention. The inverse

micelle method has been employed since the late 1980s for the preparation of both

semiconductor and metal NCs. Although it is widely adopted, samples approaching

the desired $\sigma \leq 5\%$ are rarely observed. However, Pileni and co-workers

provide a notable exception by coupling the initial synthesis with extensive use

of size-selective precipitation to yield high quality Ag (29), AgS (30), and more

recently Co NCs **(31)**.

[0067] Higher temperature reduction of metal salts in the presence of stabilizing agents

can also be employed to produce monodisperse transition metal (e.g. Co and

Ni) NCs that do not crystallize well at room temperature (RT) **(32)**. In this

general scheme metal halides or acetates are dissolved in high-boiling inert solvents

(e.g. octylether, phenylether) along with a combination of R_3P and longchain

carboxylic acids (e.g. oleic acid). The solution of metal salts and stabilizers

is vigorously stirred and heated to ~200–250 ° C at which time a solution

containing a strong reducing agent [e.g. $LiHB(CH_2CH_3)_3$, Na naphthalide, etc] is

injected. Metal NCs nucleate and grow until the reagent is consumed. Although no

Ostwald ripening is observed, NC size is coarsely tunable by the ratio of capping

groups to metal salt. Size-selective precipitation yields NC samples with σ ~ 5%.

Progress has also been made in the preparation of monodisperse bimetallic NCs.

For example, see the work by Bradley and co-workers (33). Figure 2A–D shows

high-resolution transmission electron microscopy (HRTEM) images of some of

the NC materials that can currently be prepared and isolated.

Synthesis of Shape-Controlled CdSe

[0068] The synthesis of shape-controlled CdSe nanocrystals is among the most advanced. For

instance, the preparation of a wide range of shapes, including rods, teardrops, tetrapods, and

branched tetrapods, all made by relatively simple variations in surfactant composition and time

variation of monomer concentration, have been recently reported **(15)**. Three strategies from the prototypical CdSe system were used to produce Co nanocrystals with high crystallinity, narrow size distributions, and a high degree of shape control. In both cases, the nanocrystals are produced by the injection of an organometallic precursor into a hot surfactant mixture under inert (Ar) atmosphere.

[0069] The first lesson from CdSe is that an equilibrium spherical shape will be produced in the presence of a single surfactant under thermodynamic conditions because it minimizes surface area **(16)**. Second, anisotropic particles—nanorods—are obtained by rapid growth in a surfactant mixture (under kinetic conditions), where the different surfactants are used to selectively control the growth rates of different faces **(3)**. Lastly, in both systems it is desirable to separate nucleation from growth via a rapid injection of the precursor. Tight size distributions can be obtained spontaneously when monomers can exchange between the particles under conditions of "size distribution focusing" **(16)**. Co is a more challenging system than CdSe because it has a richer crystal phase diagram with three nearly isoenergetic crystal structures [face-centered cubic (fcc), hexagonally close-packed (hcp), and epsilon].

[0070] Rapid injection of organometallic reagents in a hot coordinating solvent produces temporally discrete homogeneous nucleation. The decomposition and nucleation occurs rapidly upon injection. The lifetime of monomers in solution is short, and many small metal clusters (nuclei) form simultaneously. By dynamically coating the particles with a close-packed monolayer of coordinating ligand, the surfactant has the ability to control the size and shape of the growing particles. Through charge transfer, the surface tension is lowered and the growth can

be modified. In addition, the surfactant layer prevents the agglomeration of particles, allows monomers to add or subtract, passivates the nanocrystals against oxidation, and defines the minimum interparticle distance. Consistent with the ideas presented above, rods of hcp-Co are obtained in a binary surfactant mixture at early times after injection, and these rods spontaneously transform to more thermodynamically stable spheres of e-Co (9) if they are heated for a sufficient period of time. In these experiments, 0.4 to 0.8 g of $Co_2(CO)_8$ dissolved in 3 ml of o-dichlorobenzene are injected in a refluxing bath of 12 ml of o-dichlorobenzene (182°C) in the presence of 0.1 to 0.2 ml of oleic acid and 0.1 to 0.3 g of trioctylphosphine oxide (TOPO) (17). As the reaction proceeds in time, the products evolve in a predictable pattern. Thus, quenching the reaction solution after 5 to 10 s yields samples with Co nanorods. In this way, macroscopic samples of size-controlled Co nanorods were produced.

[0071] As time evolves over minutes, the high-energy hcp rod-shaped particles disappear at the expense of monodisperse spherically shaped e-Co nanocrystals. The further from equilibrium at the beginning of the reaction, the longer this process takes. Thus, 30 min were necessary to reach final equilibrium for 4 nm by 25 nm rods and up to 60 min in the case of 4 nm by 75 nm rods. Regarding the changes of the crystal structure, it is well known that for these crystal sizes, temperatures of about 200°C are enough to trigger atom diffusion and phase transitions (18). Even though the hcp structure is the most stable phase for bulk Co at room temperature, experimental data repeatedly show that e-Co is the most often found crystal structure in nanoparticles prepared by wet chemistry (4, 9). The evolution toward a spherical shape is consistent with the high surface tension that reduces the surface-to-volume ratio. The size of the

rods or the spheres appears to be determined by the ratio of surfactant to precursor, consistent with observations in CdSe rod growth as well as in other types of spherical metal nanoparticles (19, 20).

Production of Monodisperse Magnetic Colloids of Stabilized Cobalt Nanocrystals

[0072] A method for the production of monodisperse magnetic colloids (ferrofluids) of stabilized cobalt nanocrystals, based on the rapid pyrolysis of the organic precursor $Co_2(CO)_8$ in an inert (Ar) atmosphere and in the presence of an organic surfactant (oleic acid, lauric acid, trioctylphosphonic acid and oxide, pyridine, etc.) at high temperatures has been developed. These conditions lead to extremely narrow size distributions, avoiding costly size selective procedures. Colloidal solutions of Co nanocrystals are stable over months, and no evidence for the formation of CoO or Co_3O_4 has been observed by x-ray diffraction (XRD), transmission electron microscopy (TEM), or related spectroscopies (EDX, EELS).

[0073] The surfactant, by coating the particles with a close-packed monolayer of coordinating ligand, has the ability to control the size of the growing particles. In addition, it prevents their agglomeration, passivates them against oxidation, and defines the interparticle distance in the dried samples. This synthesis was carried out using standard airless procedures and commercially available reagents.

[0074] A concentrate solution of $Co_2(CO)_8$ (0.45–0.80 g in 2–3 ml of o-dichlorobenzene anhydrous) was injected in an o-dichlorobenzene anhydrous refluxing bath ~15 ml, T

5181 °C). The decomposition and nucleation occurs instantaneously upon injection. The lifetime

of atoms in solution is short leading to the simultaneous formation of many smallmetal clusters

(nuclei). The surfactant is present in the hot bath at concentrations of about 1%. Mixtures of oleic

acid, lauric acid, pure and technical trioctylphosphine have been used. Control of the bath

temperature and the surfactant composition modifies the strength of the metallic particle–

organic molecule bonding. Thus, by controlling the precursor/surfactant ratio, the reaction

temperature and injection time, the size of the spherical particles can be controlled and varied

between 3 and 17 nm. This method produces macroscopic quantities of Co single crystals that

are monodisperse within the limit of atomic roughness. These particles are stable in air.

Hollow Nanoparticles

[0075] Carbon buckyballs are only one example of hollow nanoparticles. Up to now, more than

30 other materials which are similarly layered were prepared as hollow nanoparticles (either

spherical or cylindrical), including, e.g., the metal dichalcogenides MX_2 (M=W, Se, X=S, Se),

BN, GaAs, and CdSe [14]. In fact, the formation of closed structures is generic for anisotropic

layered materials of finite size due to the line tension resulting from dangling bonds. Effective

pair potentials for such hollow nanoparticles are isotropic for spherical shapes, but still depend

on their radius R and thickness h. In particular, for carbon onions and hollow metal

dichalcogenides nanoparticles (inorganic fullerenes) the thickness h can vary because the

particles are multiwalled. Carbon onions with hundreds of shells have been observed

[15]. Onions are formed by metal dichalcogenides with up to 20 shells [16]. In both cases, outer

radii R can reach 100 nm, that is several orders of magnitude more than buckyballs

with R=3.55 Å .

Modified Polyol Process

[0076] The so-called modified "polyol" process has been used for preparation of bi- and trimetallic magnetic nanocrystals.[29-31,33,34] In all cases, the reduction of platinum acetylacetonate with a long-chain polyol in the presence of stabilizers was combined with the simultaneous thermal decomposition of cobalt or iron carbonyl. As a result, alloyed particles with a narrow distribution were obtained. Farrell et al.[54] used tiny particles of platinum as nuclei for further synthesis of monodisperse iron particles. Afterwards, the metallic platinum particles are not extracted from the solution and investigated.

[0077] A two-stage procedure for the preparation of bimetallic Pt@Co particles has been developed. Pure platinum particles with definite diameter were formed at first. Later, decomposition of cobalt carbonyl on the Pt seeds, if carried out at relatively low temperature, aborts formation of any alloy yielding only Pt-core/Co-shell particles. A typical synthesis is described in detail below.

[0078] In a three-necked round-bottom flask, a solution of platinum acetylacetonate (99.99%, Aldrich, 0.05 g or 0.125 mmol), 1,2-hexadecanediol (90%, Aldrich, 0.1 g or 0.38 mmol), oleic acid (99+%, Aldrich, 40 µL or 0.125 mmol), and oleylamine (70%, Aldrich, 56 µL or 0.175 mmol) in 5 mL of diphenyl ether (dpe) was heated to 205 °C. After heating for 60 min, the dark mixture was cooled to 142 °C, and the solution of the designed amount of dicobalt octacarbonyl $Co_2(CO)_8$ (contains 1-5% hexane as stabilizer, Alfa Aesar) in dpe was gradually added under a nitrogen atmosphere. Mixing and heating at this temperature was then continued for 30 min. The resulting dispersion was left to cool to room temperature, and ethanol was added to precipitate

the particles. After removal and drying of the supernatant, the magnetic particles were redispersed in toluene. Use of other nonpolar solvents such as hexane, octane, or chloroform is possible as well.

[0079] The structure of the particles was assessed by a transmission electron microscope Philips 12CM, operating at 120 kV, which was equipped with an X-ray fluorescent analyzer for the determination of the material compositions. Samples were prepared by drying a drop of the solution on a thin (5 nm) carbon-film-covered copper grid. The size distribution of the particles was measured from TEM images with at least 200 particles. The UV-visible spectra were recorded on a Bruins spectrophotometer with correction for toluene background absorption. The magnetic measurements were made on a commercial superconducting quantum interference magnetometer (SQUID) from Quantum Design for the M-H loops and from SHE for susceptibility measurements. M-H loops were taken for samples prepared by drying several drops of solution on a Si/SiO2 substrate, while the zero-field-cooled (ZFC) and field-cooled (FC) data were taken for the liquid solution.